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REACTIONS OF FREE RADICALS WITH NITRO-COMPOUNDS AND NITRATES

Final Technical Report

by

L.F. Salter and B.A. Thrush

31 March 1981

EUROPEAN RESEARCH OFFICE

United States Army

London, W.1., England

Contract Number DAERO-77-G-015

University of Cambridge,
Department of Physical Chemistry,
Lensfield Road, Cambridge
CB2 1EP. England.

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ABSTRACT

A discharge-flow system has been used to study the reaction of oxygen atoms with methyl nitrate, ethyl nitrate, nitromethane and nitroethane. In each case the initial attack involved abstraction of a hydrogen atom from the α -position. The pre-exponential factors were 1.5×10^{10} and $3 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ for the methyl and ethyl compounds respectively. The activation energies were all within 1 kJ mol^{-1} of 22 kJ mol^{-1} although the fragment derived from the nitrates but not from the nitro-compounds could undergo exothermic rearrangement. Product analyses and computer modelling were undertaken, these provided a clear explanation of why the nitro-compounds but not the nitrates are readily decomposed by a free-radical chain mechanism.

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INTRODUCTION

Aliphatic nitrates and nitro-compounds, which are extensively used as explosives, yield a wide range of products both under slow thermal decomposition¹⁻³ and under explosive conditions⁴⁻⁶. These processes must involve free radical reactions and clear evidence of the importance of kinetic as distinct from thermodynamic criteria is provided by the alkyl nitrites (RONO) which are thermodynamically less stable than the isomeric nitrocompounds (RNO₂) but unlike them do not detonate. The rates of free radical reactions must also determine the stability and safety of these substances under storage conditions.

Although the Arrhenius parameters for the initial bond rupture in the pyrolyses of simple alkyl nitrites, nitrates and nitro-compounds are well established



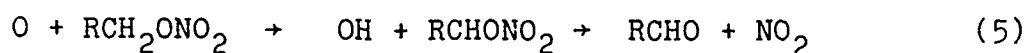
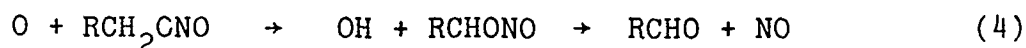
it is not possible to deduce unique mechanisms for the decomposition of such compounds by kinetic studies of the slow pyrolyses combined with product analyses. This difficulty is well illustrated by the work of Levy² who found that ethoxy radicals generated by the pyrolysis of diethyl peroxide do not accelerate the decomposition of ethyl nitrate, although the thermal decomposition of the latter undoubtedly yields ethoxy radicals which are known to be highly reactive.

In the present investigation we have used a fast flow

system to study rapid free radical reactions involving alkyl nitrites, nitrates and nitro-compounds and their degradation products. The methyl and ethyl compounds were selected as parent molecules to limit the complexity of the subsequent reactions. Atomic oxygen was chosen as the free radical species because decomposition of the parent molecule will yield oxidising radicals and because sufficient is known about the reaction of atomic oxygen to simplify the interpretation of the subsequent reaction steps.

One particularly important feature which has emerged from this study was the observation that the abstraction of a hydrogen atom from an alkyl nitrite or nitrate molecule yields a species which decomposes exothermically to yield two stable molecules.

The reactions



can be contrasted with the normal attack of the diradical, O_2 , on a hydrocarbon which yields an alkyl radical, R , which can continue the chain reaction.



Thus the reaction of a free radical with an alkyl nitrite or nitrate is essentially a chain terminating process, although the energy released in the second stage would assist the development of a thermal explosion. In contrast, the abstraction of a hydrogen atom from an alkyl nitrocompound yields a radical species $RCHNO_2$ which cannot directly split

to give two stable species. This difference of behaviour manifested itself as a chain reaction between atomic oxygen and nitrocompounds which occurred at high concentrations of the latter. Because the additional free radical species involved could not be observed directly, an attempt was made to identify the reaction mechanism by computer modelling.

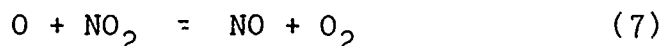
Experimental Methods

Figure 1 shows the low pressure fast flow apparatus which was used to study the reaction of oxygen atoms with methyl nitrate, ethyl nitrate, nitromethane or nitroethane. The reactor consisted of a 25 mm diameter pyrex tube which passed through a copper-lined electric furnace which was 900 mm long. The furnace temperature was controlled by a Eurotherm regulator.

The reaction time could be varied by introducing the alkyl nitrate or nitro-compound at different points along the flow tube through a grease-less movable injector system. The reagent was fed through fine Tygon tubing into a narrow-bore glass tube which terminated in a fine jet. This glass tube was slid along the flow tube by a frictional drive from a rotating shaft which passed through a cone and socket joint. Reaction times of 0.02 to 1.0 s could readily be obtained with total pressures in the range 1 - 10 Torr.

Atomic oxygen was generated by passing ca 1% of molecular oxygen in an argon carrier through a 200 W, 2450 MHz microwave discharge. Concentrations of atomic oxygen were measured

using the stoichiometric titration reaction



using an R.C.A. 1P28 photomultiplier cell to measure the intensity of the air afterglow produced downstream from the furnace exit where the flowing gases had completely cooled to ambient temperature. The intensity of the air afterglow is given by

$$I = I_0 [\text{O}] [\text{NO}] \quad (\text{i})$$

When nitrogen dioxide is introduced through the mixing jet at the furnace exit, the maximum intensity of the air afterglow is observed when half the oxygen atoms have been converted to nitric oxide by reaction (7). Thus

$$I_{\text{MAX}} = I_0 [\text{O}]_0^2 / 4 \quad (\text{ii})$$

where $[\text{O}]_0$ is the initial oxygen atom concentration, providing an absolute calibration for the photomultiplier cell based on the titration reaction (7). Knowing I_0 , it is then possible to measure the concentration of oxygen atoms before and after addition of an alkyl nitrate upstream, as well as the amount of nitric oxide formed in the decomposition of the alkyl nitrate. This is achieved by adding known flows of nitric oxide at the furnace exit and using relation (i) in the form

$$I = I_0 [\text{O}] ([\text{NO}]_f + [\text{NO}]_{\text{added}}) \quad (\text{iii})$$

A plot of I against $[\text{NO}]_{\text{added}}$ is a straight line with slope $I_0[\text{O}]$, and intercept on the abscissa equal to the flow of nitric oxide emerging from the furnace $[\text{NO}]_f$.

Purification of Reagents

A commercial sample of methyl nitrate of nominal purity 99.8% was distilled at 193K, the initial and final fractions being discarded. The liquid was then subjected to several freeze-pump-thaw cycles followed by direct pumping at room temperature immediately prior to use. Ethyl nitrate was supplied by the Explosives Research and Development Establishment (Waltham Abbey) and was purified in a similar manner. Similar purification methods were used for commercial samples of nitromethane and of nitroethane except that the vacuum distillations were carried out at 273K.

Nitrogen dioxide (Matheson) was purified by successive distillation using traps at 77K and 193K. This was continued until the solid was pure white, indicating that water and other nitrogen oxides were not longer present. It was stored in a blackened bulb.

Nitric oxide (Matheson) was purified by distillation in vacuo from 90K to 77K and from 113K to 77K through a trap containing molecular sieve and soda lime cooled to 113K.

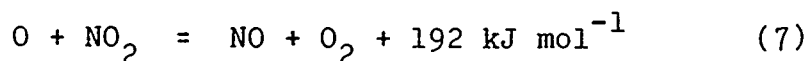
Oxygen and argon were purified by passage through two traps at 193K and atmospheric pressure packed with glass wool followed by a similar trap at 77K and reduced pressure. Technical grade carbon monoxide (B.O.C.) was purified by passage over silica chips at 670K and then through silica gel in a U-tube and a trap containing glass wool, both at 196K. It was then passed at reduced pressure through a trap at 77K containing glass wool.

Gas flows were measured using conventional capillary

flow meters: the calibration of these was based on, but did not assume, the validity of Poiseuille's Law.

Experimental Procedure

In the previous study⁸ of the reactions of methyl nitrite and of ethyl nitrite with atomic oxygen, it was shown that the initial attack was the slowest step and that the species produced reacted relatively rapidly with more atomic oxygen to yield the final products, in which the nitrogen of the initial molecule appeared solely as nitric oxide. A similar situation would be expected to obtain in the reaction of atomic oxygen with methyl nitrate or ethyl nitrate, since any nitrogen dioxide produced would rapidly be reduced to nitric oxide by the excess oxygen which was invariably present



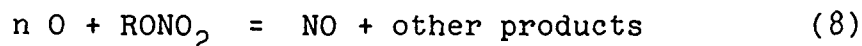
$$k_7 = 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (\text{ref.9})$$

Thus measurement of the number of oxygen atoms consumed per nitric oxide molecule formed gives the stoichiometry (n) of the reaction between oxygen atoms and an alkyl nitrate.

That is

$$n = ([\text{O}]_0 - [\text{O}])/[\text{NO}]_f \quad (\text{iv})$$

where the overall reaction is



Providing the subsequent reactions are rapid, the rate constant k for the initial attack of an oxygen atom on an alkyl nitrate molecule can then be derived from the integrated rate expression

$$\ln \frac{[O] [RONO_2]_0}{[O]_0 ([RONO_2]_0 - x)} = ([O]_0 - n[RONO_2]_0)kt \quad (v)$$

where $nx = [O]_0 - [O]$.

Experimentally, it is simplest to vary the nitrate concentration for a fixed reaction time. It should be noted that any contribution by atoms or free radicals produced in the reaction to the initial attack on the alkyl nitrate molecule will increase the nitric oxide yield, reduce the measured stoichiometry n and hence increase the value of k derived from relation (iv).

Results

Reaction of Oxygen Atoms with Methyl Nitrate

The kinetic behaviour of the reaction of oxygen atoms with methyl nitrate closely resembles that of the reaction of oxygen atoms with methyl nitrate⁸. The measured reaction stoichiometry is close to 6 and decreases with increasing substrate flow due to reactions between product radicals and methyl nitrate (figure 2).

Since both the mechanisms discussed below give stoichiometries of $n = 6$, the limiting values of the rate coefficient at low methyl nitrate concentrations were calculated for $n = 6$. These are given in Arrhenius form in figure 3, where the best straight line corresponds to the rate expression

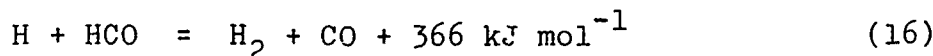
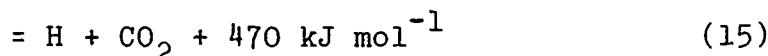
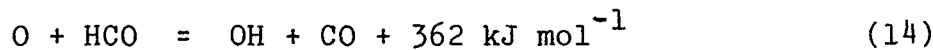
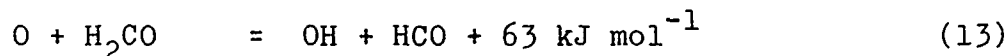
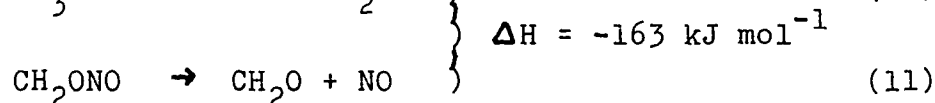
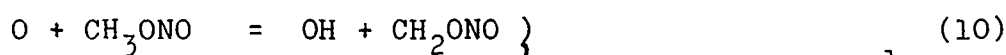
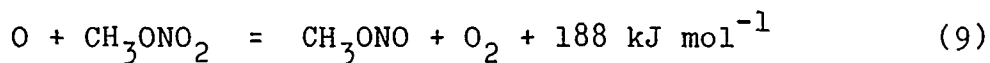
$$k = 1.3 \times 10^{10} \exp(-21.6 \text{ kJ mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

For the reaction of oxygen atoms with methyl nitrite, a closely similar value was obtained for the corresponding Arrhenius expression⁸

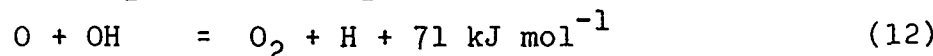
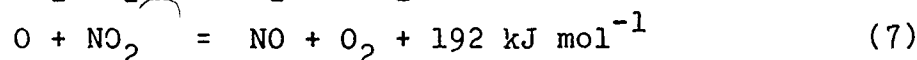
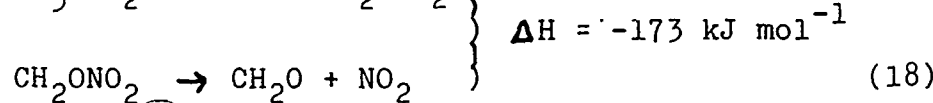
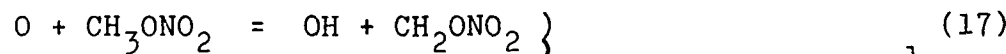
$$k = 1.4 \times 10^{10} \exp(-21.8 \pm 2.0 \text{ kJ mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

There are two mechanisms for the reaction between oxygen atoms and methyl nitrate which would give the required stoichiometry of $n = 6$ and are basically consistent with the previous results on the reaction of oxygen atoms with methyl nitrite and other compounds^{8,10,11}.

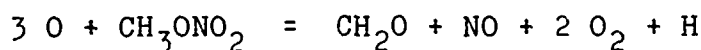
If the initial step involves abstraction of an oxygen atom from the methyl nitrate, the reaction of oxygen atoms with methyl nitrite which has an overall stoichiometry of $n = 5$ would follow :



The other mechanism starts, like the methyl nitrite reaction, with hydrogen abstraction



In both mechanisms, the reaction of oxygen atoms with methyl nitrate and the subsequent steps give the stoichiometry



This is followed by the reaction of oxygen atoms and formaldehyde which goes virtually to completion since its initial step (13) has a rate coefficient more than ten times that found here for the reaction of oxygen atoms with methyl nitrate ($k_{13} = 9 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300K^{11}). This reaction and the subsequent rapid steps (12), (14), (15) and (16) give an observed stoichiometry of $n = 2.8$, making the overall reaction stoichiometry close to $n = 6$ for both mechanisms.

The measured Arrhenius parameters of the overall reaction are almost identical to those previously found⁸ for reaction (10). If this measured rate coefficient corresponded to reaction (9), then the fractional extent of reaction (10) cannot exceed that of reaction (9) and the stoichiometry of the overall reaction would be much less than $n = 6$, since oxygen atoms are mainly consumed in steps subsequent to (10). On the other hand, if reaction (9) were rapid and (10) were the rate determining process, then a rapid reaction with stoichiometry $n = 1$ would have been detected in the kinetic studies, particularly those at room temperature where reaction (10) is slow.

If, as appears highly probable, the C-H bond strengths in methyl nitrite and methyl nitrate are closely similar, then reactions (17) and (10) would be expected to have virtually identical Arrhenius parameters as is found experimentally for the overall reactions of oxygen atoms with methyl nitrite and with methyl nitrate. We therefore conclude that the initial step in both these reactions is hydrogen abstraction. For reaction (17), the A-factor found experimentally (1.3×10^{10}

$\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) agrees within the error limits with the value of $1.5 \times 10^{10} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ predicted from experiments on a series of primary alkanes¹², thus we adopt that value for the A-factor giving

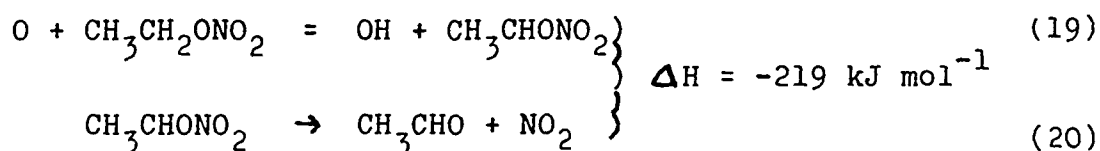
$$k_{17} = 1.5 \times 10^{10} \exp(-22.0 \pm 1.0 \text{ kJ mol}^{-1}/RT) \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$$

where the error limits correspond to two standard deviations of the activation energy with a predetermined A-factor.

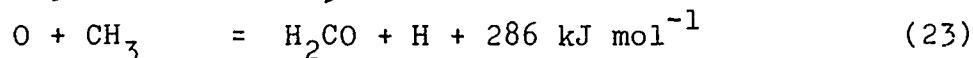
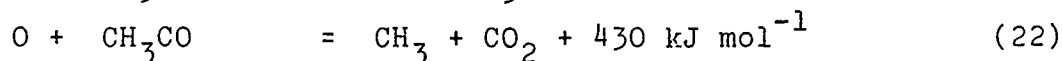
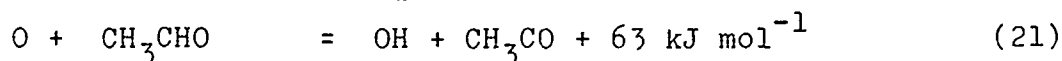
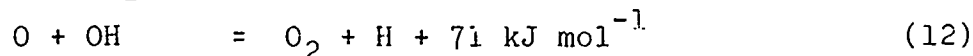
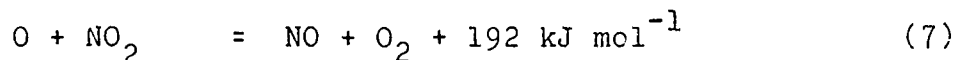
Reaction of Oxygen Atoms with Ethyl Nitrate

As observed in the previous study of ethyl nitrite⁸, the presence of an additional CH_2 group increases the number of oxygen atoms removed per initial step. Although the greater rate of the reaction of ethyl nitrate with oxygen atoms made it possible to use lower concentrations than those of methyl nitrate, the measured stoichiometries of nitric oxide production still rose quite sharply at low ethyl nitrate concentrations. These gave intercepts corresponding to $n \approx 10$ at zero reactant concentration as shown in figure 4. Thus the observed difference between the stoichiometries of the reactions of oxygen atoms with methyl nitrate and ethyl nitrate are the same as with the corresponding nitrites⁸.

This, and the increase in rate of the initial step on passing from the methyl to the ethyl derivative, which was also observed with the nitrites⁸, leads to the conclusion that the mechanism of the reaction of oxygen atoms with ethyl nitrate is strictly analogous to the reaction with ethyl nitrite, the mechanism being



(20)



followed by the reaction of oxygen atoms with formaldehyde discussed above. Since $k_{21} = 3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300K^{12} , which is thirty times faster than the rate coefficient found here for reaction (19), the reactions of oxygen atoms with acetaldehyde and formaldehyde would go to completion on the time scale of the present experiments. The predicted overall stoichiometry for this reaction sequence is $n = 10$, which agrees with the measured value well within its limited accuracy.

The limiting values of the rate coefficient of the initial step at low ethyl nitrate concentrations were evaluated for $n = 10$. These are plotted in Arrhenius form in figure 3. As with methyl nitrate, the accuracy with which the preexponential factor could be determined was not high. The predicted value of $2.6 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for two secondary hydrogens¹³ was adopted since it lay in the centre of the possible range of experimental values.

The Arrhenius expression is then

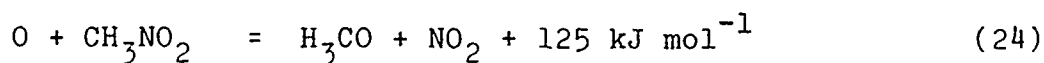
$$k_{19} = 2.6 \times 10^{10} \exp(-21.6 \pm 2.6 \text{ kJ mol}^{-1}/RT) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Reaction (19) is more than three times faster than reaction (17), partly due to a smaller activation energy.

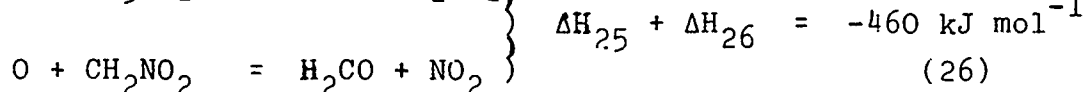
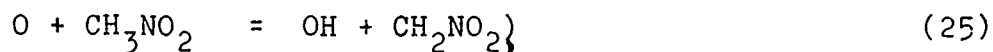
Reaction of Oxygen Atoms with Nitromethane

The kinetic behaviour of the reaction of oxygen atoms with nitromethane resembles that of the reaction of oxygen atoms with methyl nitrite⁸ and methyl nitrate. The measured limiting reaction stoichiometry is close to 7 (oxygen atoms removed per nitromethane molecule) and decreases with increasing substrate flow due to reactions between product radicals and nitromethane (fig.5).

On the basis of this and previous work¹⁴, two mechanisms appear possible, both giving stoichiometries $n = 7$. These differ in the initial mode of attack. One mechanism is



and the other begins



and is also followed by steps (12) to (16) and (7).

In both these mechanisms the two initial steps yield OH and NO₂ which react rapidly with O, giving a stoichiometry of 4. The subsequent reaction of oxygen atoms with formaldehyde¹¹, which is fifty times faster than the initial step, has a measured stoichiometry of 2.8 giving an overall stoich-

iometry close to the measured value of 7.

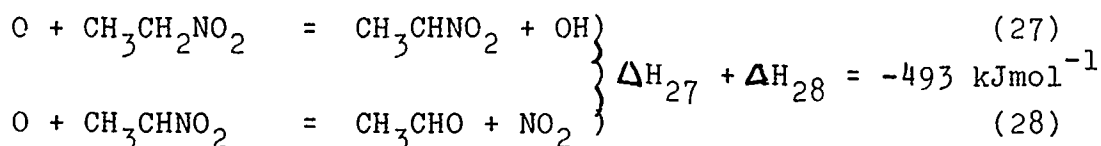
The observed Arrhenius parameters for the initial reaction agree well with those predicted for the abstraction of hydrogen by atomic oxygen from a series of primary alkanes¹³ and are also virtually identical with those observed for the reaction of oxygen atoms with methyl nitrite⁸ and methyl nitrate. It seems reasonable to conclude that reaction (25) is the initial step, with k_{25} given by

$$k_{25} = 10^{(10.18 \pm 0.27)} \exp(-22.4 \pm 1.8 \text{ kJ mol}^{-1}) / RT \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The error limits correspond to two standard deviations from the straight line in fig.6 and at 295K this expression gives $k_{25} = 1.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; in fair agreement with the value of $1.9(\pm 0.3) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ reported previously.¹⁴

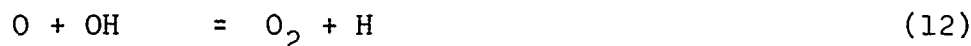
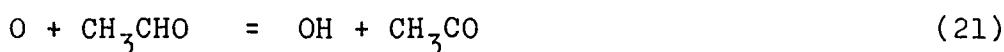
Reaction of Oxygen Atoms with Nitroethane

The observed stoichiometry (fig.7) for the reaction of oxygen atoms with nitroethane approaches a limiting value of ~ 1.1 at low substrate concentration. The stoichiometry plot for nitroethane rises more sharply towards the limit than the corresponding plot for nitromethane; this behaviour was also observed for the similar plots of ethyl nitrite⁸ and nitrate when compared to their methyl analogues; the difference probably arises from the greater number of free radical species (e.g., OH, H) produced from fragmentation of ethyl derivatives as compared with the methyl derivatives. As in the previous studies a slightly lower activation energy for the ethyl derivative is also observed here, supporting the analogous mechanism



(27)

(28)



followed by reactions (13) to (16) between oxygen atoms and formaldehyde. This mechanism gives an overall stoichiometry of $n = 11$ and the reactions of oxygen atoms with the intermediate molecules H_2CO and CH_3CHO are both more than ten times faster than the initial step at 300K.^{11,12} Incorporating this stoichiometry into the rate equation yields the Arrhenius plot shown in fig.6 where the best straight line gives

$$k_{27} = 10^{(10.50 \pm 0.96)} \exp(-22.2 \pm 7 \text{ kJ mol}^{-1}) / RT \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

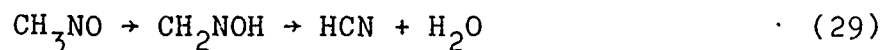
The error limits quoted are two standard deviations from the straight line in fig.6.

Products from Nitrocompounds.

Unlike the alkyl nitrites and nitrates, the nitro compounds contain a C-N linkage which might partially survive free radical attack. An attempt was, therefore, made to identify some of the products of the oxygen atom-nitroalkane reaction. It was difficult to obtain sufficient amounts of material for analysis whilst maintaining the conditions for which secondary reactions were minimized, i.e. low substrate

concentration and short reaction times. For gas chromatographic analysis a trap at 196K was placed at the end of the flow tube and the product collected. The reliability of these analyses, performed after some hours of continuous sampling, should be viewed with caution, since some subsequent reaction could have occurred in the cold trap.

For nitromethane a portion of the gas-flow was bubbled through alkaline aqueous ferrous sulphate and the "Prussian Blue" test¹⁵ for hydrogen cyanide performed. This sensitive test could not detect the presence of hydrogen cyanide amongst the products of reaction showing that hydrogen cyanide represents <0.1% of the reaction products. A similar result was obtained with both infrared and gas chromatographic¹⁶ analysis of the condensed products. The absence of hydrogen cyanide indicates that the C-N bond in nitromethane does not survive oxygen atom attack under these conditions and that no CH_3NO is formed, since this molecule yields hydrogen cyanide via reaction (29);¹⁷



It is also possible that the attack of oxygen atom on any nitrosomethane present would also yield hydrogen cyanide.

Formaldehyde was not found in the gas chromatographic analysis of the products, but this is thought to reflect both the low steady state concentration of formaldehyde ($k_{13} \sim 50k_{25}$ at 300K) and the ease with which formaldehyde undergoes polymerization on a cold surface [see for instance, ref.(18)], rather than its absence as a primary product. It is also possible that formaldehyde reacts with unconverted nitromethane in the condensed phase¹⁶ to give a variety of products

in quantities too small for gas chromatographic detection.

For nitroethane, gas chromatographic analysis of the collected products indicated that acetaldehyde was present as the dominant condensible product at short reaction times.

No other products were found in quantities large enough for unambiguous identification in agreement with the suggested mechanisms which do not include any other condensible products which would give a signal with flame ionization detection.

As reported previously for nitromethane,¹⁴ a considerable acceleration in the rate of reaction of nitromethane, or nitroethane, and atomic oxygen is observed at high substrate concentrations and long reaction time. This results in complete consumption of the atomic oxygen and is almost certainly due to a chain reaction between oxygen atoms and the nitrocompounds. Under these conditions trace amounts of organic products but no hydrogen cyanide were just detectable in the products from the nitromethane reaction, whilst for nitroethane the compounds methyl cyanide, methanol, ethanol and acetone were identified as products in addition to acetaldehyde. As expected, the product sampling technique permits only a qualitative examination of the system, but the presence of methyl cyanide shows that under these extreme conditions C-N bond rupture is not involved in every reactive encounter of a nitroethane molecule. The variety of organic products also suggests the occurrence of a different mechanism from that in the "low substrate concentration-short reaction time" regime used for the kinetic studies reported above.

Effect of Carbon Monoxide on Chain Reaction

At elevated temperatures and at higher concentrations of the nitro-alkane, observations of the air-afterglow established that there was a clearly defined extinction point due to complete consumption of atomic oxygen. This was wholly different from the normal reaction at low nitro-alkane concentration which was first order in both reagents. This phenomenon was investigated by adding sufficient carbon monoxide to the system largely to replace the reaction



by the reaction

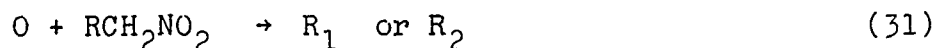


which also converts OH to H but without removing oxygen atoms.

In these experiments, the added carbon monoxide was always replaced by an equal flow of nitrogen to conserve both flow rate and total pressure. As expected, large additions of carbon monoxide reduced the consumption of atomic oxygen causing the chemiluminescence to reappear downstream. Measurement of the intensity distribution of this chemiluminescence using calibrated filters in front of the photomultiplier cell showed that it consisted of the air afterglow plus carbon monoxide flame band emission which is associated with the chemiluminescent combination of O and CO.¹⁹

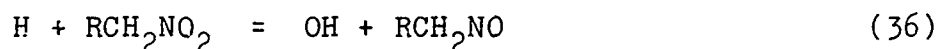
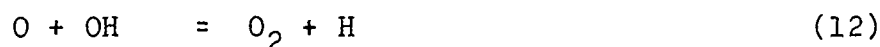
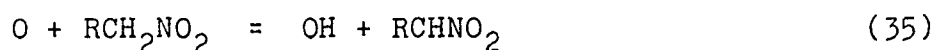
The effect of carbon monoxide on the chain reaction between nitroethane and a fixed concentration of atomic oxygen is shown in figure 8. The amount of nitroethane needed to produce a sharp extinction of the chemiluminescence rises by a factor of two as carbon monoxide is added and then stays remarkably constant for larger additions of carbon monoxide.

A chain reaction between oxygen atoms and a nitro-alkane should have the general form

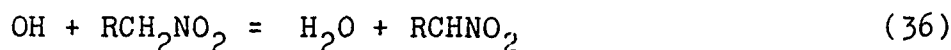
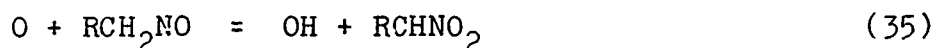


Two possible identities for the radicals R_1 , R_2 appear plausible:

(a) If $R_1 = OH$ then $R_2 = H$ giving the initial steps



(b) If $R_2 = OH$, then R_1 must have a highly abstractable hydrogen and the chain reaction will occur at high ratios of nitro-alkane to atomic oxygen where reaction (36) can compete with reaction (12):



In the first case, the addition of CO will reduce the consumption of atomic oxygen because reaction (12) is replaced by reaction (30) which also converts OH to H, but without consuming atomic oxygen. The second case is less clear-cut because reactions (30) and (36) yield different

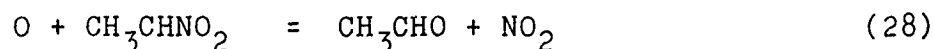
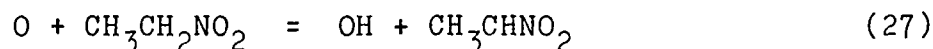
radicals, but the effect of CO addition must also be a reduction in the consumption of nitro-alkane. However, the rate coefficients of reactions (12), (30) and (36) are known^{20,21}, and it is possible to calculate the extent to which these processes compete with each other in the present system. When sufficient CO has been added to give half its maximum effect on the chain reaction, the rates of consumption of OH by the three routes at 296K are:-

$$\begin{aligned} k_{12}[\text{O}] &= 900 \text{ s}^{-1} \\ k_{30}[\text{CO}] &= 1800 \text{ s}^{-1} \\ k_{36}[\text{EtNO}_2] &= 80 \text{ s}^{-1} \end{aligned}$$

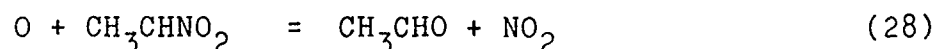
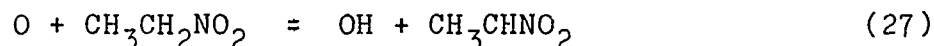
Under these conditions reactions (12) and (30) are clearly competing with each other. It follows that reaction (12) is the main process removing OH in the absence of CO, and that mechanism (a) obtains in this system.

The increased amounts of nitroethane needed to cause the reaction with atomic oxygen to go to completion in the presence of CO must be associated with the decreased consumption of atomic oxygen since reactions (12) and (30) both convert the radical OH to the radical H, but (30) unlike (12) does not consume atomic oxygen. The factor of two increase in the initial nitroethane concentration for chain consumption of atomic oxygen therefore suggests that, under these conditions, half the atomic oxygen is removed by reaction (12). Such conditions correspond to much higher initial ratios of nitroethane to atomic oxygen than were used to study the kinetics of the reaction between these species, and figure 7 shows that they correspond to a reaction stoichiometry of $4 \text{ O} + \text{C}_2\text{H}_5\text{NO}_2$ for complete consumption of atomic oxygen in the absence of CO.

Neglecting the subsequent reaction of atomic oxygen with acetaldehyde¹², the reaction sequence



provides the correct stoichiometry, but only removes one quarter of the atomic oxygen by reaction (12). However, atomic hydrogen reacts 15 times faster with NO_2 than does atomic oxygen²², and since reaction (12) yields atomic hydrogen, the above mechanism will be replaced at a very early stage by the stoichiometrically equivalent sequence



In this mechanism, half the atomic oxygen is consumed by reaction (12) with OH as deduced above from the limiting effect of CO addition, providing a satisfying interpretation of the observations.

The most rapid reaction of the product acetaldehyde would be with hydroxyl radicals; however, the rate coefficient for this process is one quarter that of reaction (12).²³ Since the maximum yield of acetaldehyde is one quarter of the oxygen atoms consumed, the contribution of the $\text{OH} + \text{CH}_3\text{CHO}$ to consumption of OH radicals will not have a significant effect on the deductions made here. Any attempt to understand the detailed mechanism including the breakdown

of acetaldehyde involves such a large number of reactions that computer modelling is required. A preliminary study involving 35 reactions, half with known rate coefficients and half with estimated ones, which leads to agreement with the experimental observations is described briefly in appendix A.

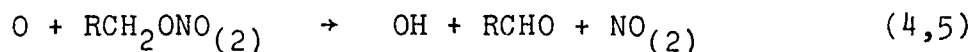
DISCUSSION

Herron and Huie¹³ have shown that the activation energies for hydrogen abstraction from paraffin hydrocarbons by atomic oxygen show a linear dependence on the strength of the bond broken:

$$E_a = 0.36 D(C-H) - 343 \text{ kJ mol}^{-1}$$

If one assumed that this also applies to the C-H bonds in alkyl nitrites, nitrates and nitro-compounds, the results summarised in table 1 show that these C-H bond energies must all be close to 405 kJ mol^{-1} . These bond energies are similar to the primary and secondary C-H bond energies in alkanes, and there is no evidence in the present work that the proximity of a nitrite, nitrate or nitro- group affects the energy of the proximate C-H bonds. (It should also be noted that the observed pre-exponential factors (table 1) are consistent with those expected for an abstraction reaction of oxygen atoms involving three primary or two secondary hydrogen atoms for methyl and ethyl compounds respectively.)

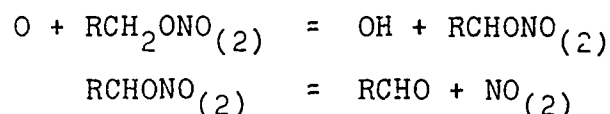
In the case of the nitro-compounds, this conclusion about bond energies is unremarkable, but the overall reactions for the nitrites and nitrates.



are some 160-220 kJ mol⁻¹ exothermic whereas the corresponding reaction of an alkane

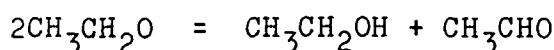


is almost exactly thermoneutral. This shows clearly that reactions (4) and (5) must be regarded as two stage processes, in which the initial abstraction of hydrogen precedes the exothermic rupture of the fragment produced, and that the energy released in this fragmentation is not available to reduce the activation energy of the initial step:-

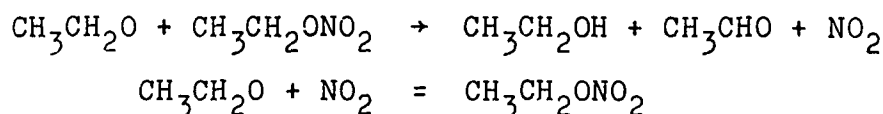


This mechanism would also be expected to apply to the reactions of hydrogen atoms, hydroxyl radicals and alkoxy radicals with alkyl nitrates and nitrites. With these mono-radicals all the products are stable molecules. This explains why alkyl nitrites and nitrates are relatively stable molecules at and above room temperature despite the easy fission of the RO-NO₍₂₎ bond to yield the highly reactive alkoxy radical.

The observation by Levy² that ethoxy radicals do not catalyse the decomposition of ethyl nitrate is simply explained by the reaction



being replaced by



which have identical products.

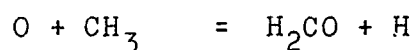
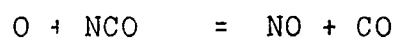
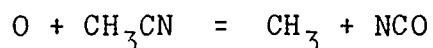
Hydroxyl radicals react with nitromethane and with methyl nitrite at similar rates $(5.5 \pm 0.6) \times 10^8$ and $(8.0 \pm 1.1) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 292K²¹. These rate coefficients are both about 100 times faster than for the corresponding reactions of atomic oxygen. This is to be expected since the reactions $\text{RH} + \text{OH} = \text{R} + \text{H}_2\text{O}$ is 71 kJ mol^{-1} more exothermic than the corresponding reaction $\text{RH} + \text{O} = \text{R} + \text{OH}$. This provides further evidence that hydrogen atom abstraction is the primary mode of radical attack on these molecules. The essential difference between these reactions for nitrites and nitrates on the one hand and the nitro-compounds on the other is that for the former species, the radical R breaks up exothermically to yield stable species whereas in the latter case such a process would require a complex rearrangement of bonds. It is therefore not surprising that the reaction of atomic oxygen with nitromethane and with nitroethane becomes a chain reaction under some conditions whereas the reactions of the nitrites and nitrates do not.

The experiments in which carbon monoxide was added to scavenge hydroxyl radicals provided clear evidence that this species is a chain carrier in the reaction between atomic oxygen and nitroethane. An attempt was therefore made to model this chain reaction on an IBM 370/165 computer using step wise integration with the NAGLIB D02AEF programme. Under the conditions used here to determine the rate coefficient of the $\text{O} + \text{CH}_3\text{CH}_2\text{NO}_2$ reaction, the main fate of its primary product, CH_3CHNO_2 , is to react with atomic oxygen to give the stable species CH_3CHO and

NO_2 . For a chain reaction to become established in the system, it is necessary for CH_3CHNO_2 to generate additional radical species. It is unlikely to do this by reacting with nitroethane, and it was concluded that the reaction sequence

$$\text{H} + \text{CH}_3\text{CHNO}_2 \rightarrow \text{CH}_3\text{CHNO} + \text{OH} \rightarrow \text{CH}_3\text{CN} + \text{OH} + \text{OH}$$

provided the best explanation of the overall kinetics providing that the reaction of oxygen atoms with methyl cyanide provided an additional source of free radicals:



The reaction scheme listed in appendix A was found to account well for the observed kinetic behaviour, rate of reaction and reaction products as well as for the inhibition by carbon monoxide. However it was necessary to reduce the rate coefficient of the $\text{HO} + \text{CH}_3\text{CH}_2\text{NO}_2$ reaction to one tenth of its measured value to account for the acceleration observed under the conditions of the chain reaction, which was strongly dependent on the concentration of the highly reactive OH radical. As the experimental determination of this rate coefficient is unlikely to be seriously in error, it was concluded that there must be another chain propagating reaction of the CH_3CHNO_2 reaction in addition to that with atomic hydrogen. In view of the number of reactions for which activation energies are unknown or the rate coefficients estimated, more experimental data are clearly needed before a unique reaction mechanism can be determined by computer modelling.

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Table 1

Arrhenius parameters of oxygen atom attack.

Substrate	$\text{Log}(A/\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$	$E/\text{kJ mol}^{-1}$
CH_3ONO	10.15	21.8 ± 2.0
$\text{C}_2\text{H}_5\text{ONO}$	10.41	20.3 ± 2.0
CH_3ONO	10.18	22.0 ± 1.0
$\text{C}_2\text{H}_5\text{ONO}_2$	10.42	21.6 ± 2.6
CH_3NO_2	10.18	22.4 ± 1.8
$\text{C}_2\text{H}_5\text{NO}_2$	10.50	22.7 ± 7.0

APPENDIX A

The following pages list the 35 reactions and their rate coefficients which were included in the computer model of the chain reaction between atomic oxygen and nitroethane. The reaction numbers and reference numbers in this Appendix do not correspond to those in the body of the report.

This reaction mechanism accounts for the observed kinetics, reaction rate, product distribution and inhibition by carbon monoxide. The acceleration of rate in the chain reaction is largely governed by reaction (11) which converts the highly reactive hydroxyl radical to a less active radical (CH_3CHNO_2). Very good matches of the observed behaviour were obtained by reducing k_{11} to one tenth of its measured value. As k_{11} is unlikely to be in serious error, it was concluded that reaction (21) cannot be the only process converting CH_3CHNO_2 into more active free radicals. Because the programme required 7 min. CPU time on an IBM 370/165 computer, only a limited number of computations could be made and this prevented a more detailed investigation of the reaction mechanism.

No.	Reaction	Rate constant at 293K	Reference
1	$O + CH_3CH_2NO_2 = OH + CH_3CHNO_2$	5.0 (+ 7)	3
2	$O + CH_3CHNO_2 = CH_3CHO + NO_2$	3.0 (+ 10)	E
3	$O + CH_3CHO = OH + CH_3CO$	3.0 (+ 8)	4
4	$O + CH_3CO = CH_3 + CO_2$	3.4 (+ 9)	4
5	$O + CH_3 = CH_2O + H$	2.0 (+ 10)	5
6	$O + CH_2O = OH + HCO$	9.0 (+ 7)	6
7a	$O + HCO = OH + CO$	5.7 (+ 9).	6E
7b	$= H + CO_2$	4.3 (+ 9)	6E
8	$H + HCO = H_2 + CO$	3.0 (+ 10)	6E
9	$O + OH = O_2 + H$	3.0 (+ 10)	7
10	$H + NO_2 = NO + OH$	7.8 (+ 10)	8
11	$OH + CH_3CH_2NO_2 = H_2O + CH_3CHNO_2$	5.5 (+ 8)	9
12	$O + NO_2 = NO + O_2$	5.0 (+ 9)	10
13	$O + CO + M = CO_2 + M$	1.2 (+ 2)	11
14	$OH + CO = CO_2 + H$	9.0 (+ 7)	12
15	$OH + CH_3CHO = H_2O + CH_3CO$	9.0 (+ 9)	13
16	$H + CH_3CH_2NO_2 = H_2 + CH_3CHNO_2$	1.0 (+ 7)	14E
17	$H + CH_3CHO = H_2 + CH_3\dot{C}HO$	3.0 (+ 7)	15
18	$H + CH_3CO = H_2 + CH_2CO$	1.0 (+ 10)	16E
19	$O + CH_2CO = CH_2O + CO$	3.4 (+ 8)	4
20	$CH_3 + CH_3CH_2NO_2 = CH_4 + CH_3CHNO_2$	1.0 (+ 5)	17E
21	$H + CH_3CHNO_2 = CH_3CN + 2 OH$	1.0 (+ 10)	E
22	$O + CH_3CN = CH_3 + NCO$	2.1 (+ 4)	18
23	$O + NCO = NO + CO$	1.0 (+ 10)	E
24	$H + CH_2O = H_2 + HCO$	2.6 (+ 7)	16
25	$H + CH_3CHNO_2 = CH_3CH_2 + NO_2$	3.0 (+ 10)	E
26	$CH_3CH_2 + NO_2 = CH_3CH_2O + NO$	5.0 (+ 9)	19E
27	$CH_3 + NO_2 = CH_3O + NO$	3.3 (+ 9)	19
28	$CH_3CH_2 + NO = CH_3CHNOM$	5.0 (+ 8)	19E

No.	Reaction	Rate constant at 293K	Reference
29	$\text{CH}_3 + \text{NO} = \text{CH}_2\text{NOH}$	3.0 (+ 8)	19E
30	$\text{CH}_3\text{CH}_2\text{O} + \text{CH}_3\text{CH}_2\text{NO}_2 = \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CHNO}_2$	3.0 (+ 10)	E
31	$\text{CH}_3\text{O} + \text{CH}_3\text{CH}_2\text{NO}_2 = \text{CH}_3\text{OH} + \text{CH}_3\text{CHNO}_2$	3.0 (+ 10)	E
32	$\text{CH}_3\text{CHNO}_2 + \text{CH} = \text{CH}_3\text{CHOH} + \text{NO}_2$	3.0 (+ 10)	E
33	$\text{CH}_3\text{CHOH} + \text{CH}_3\text{CH}_2\text{NO}_2 = \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CHNO}_2$	1.0 (+ 6)	E
34	$\text{OH} + \text{CH}_2\text{O} = \text{H}_2\text{O} + \text{HCO}$	9.0 (+ 9)	20
35	$\text{O} + \text{NO} + \text{M} = \text{NO}_2 + \text{M}$	1.0 (+ 8)	21

All rate constants are given in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ units; 3.0 (+ 7) means $3.0 \times 10^{+7}$.

E denotes a rate constant which has been estimated either directly or on the basis of the reference given.

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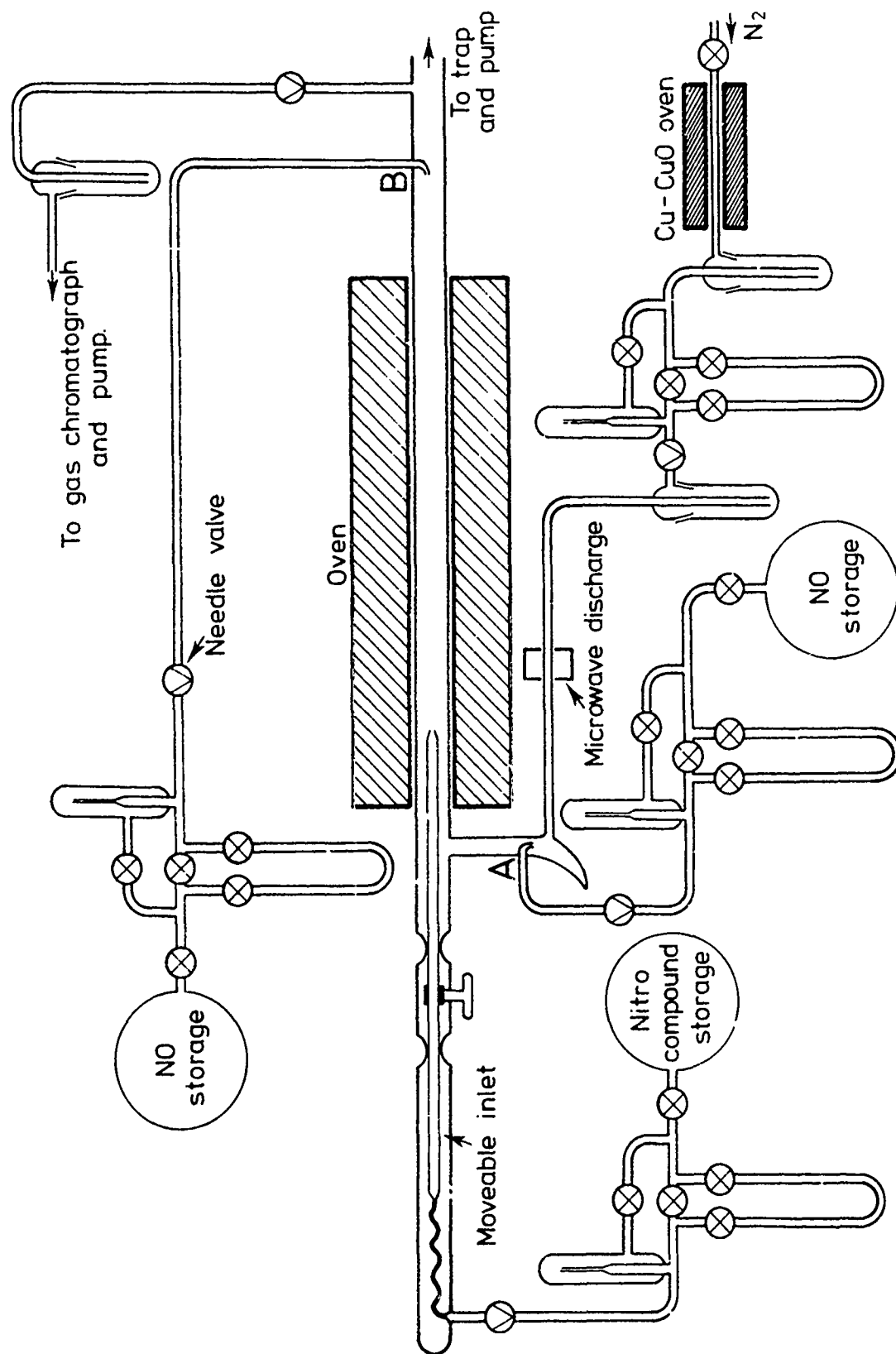


Figure 1. DIAGRAM OF FLOW APPARATUS. IN THE CONFIGURATION SHOWN, OXYGEN ATOMS ARE PRODUCED BY TITRATING NITROGEN ATOMS WITH NITRIC OXIDE AT A; FURTHER NITRIC OXIDE IS ADDED AT B TO CALIBRATE THE NITRIC OXIDE YIELDS.

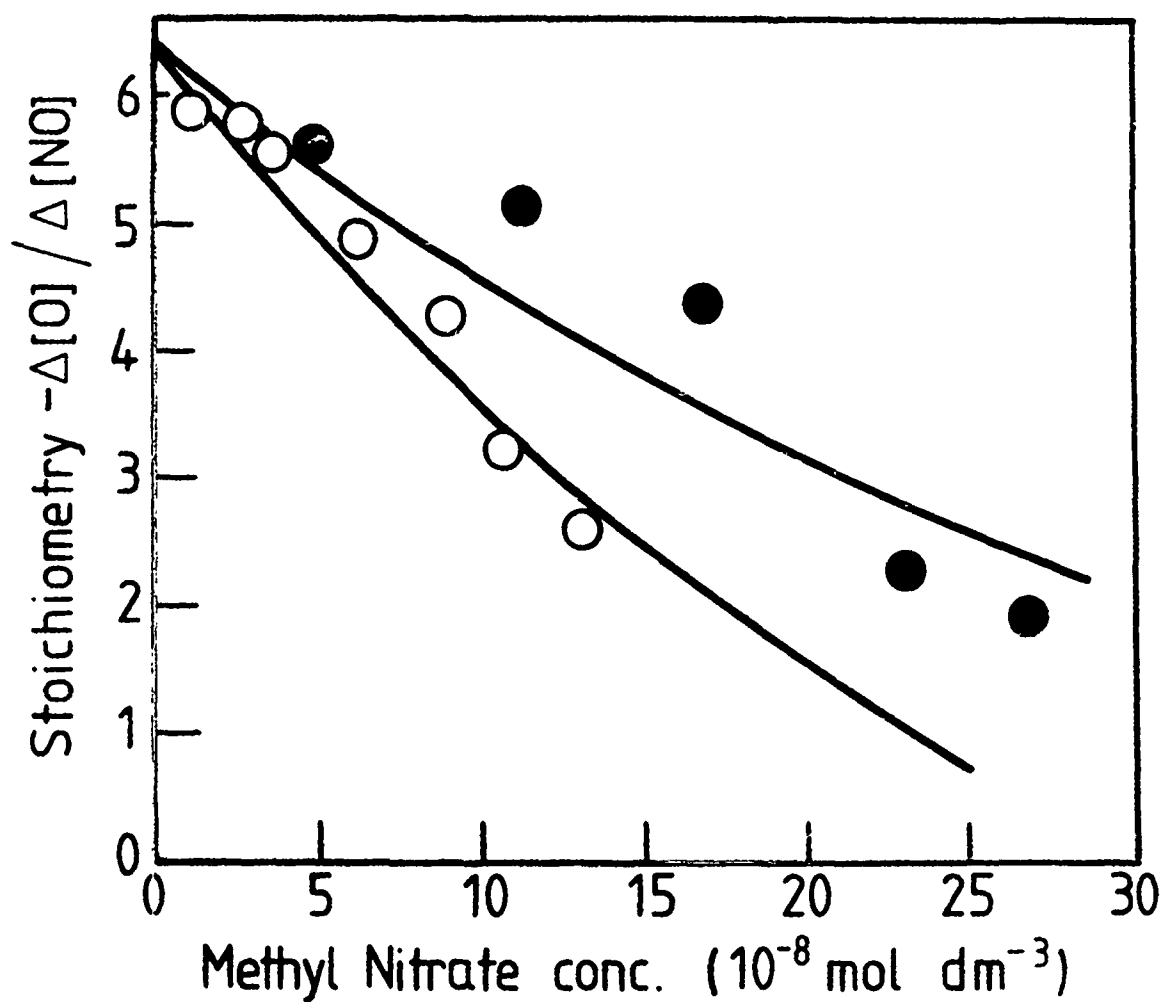


Figure 2. Full circles: 0.40 s reaction time at 294.4K;
 $[\text{O}]_0 = 9.5 \times 10^{-8} \text{ mol dm}^{-3}$
 Open circles: 0.24 s reaction time at 383.2K;
 $[\text{O}]_0 = 4.5 \times 10^{-8} \text{ mol dm}^{-3}$.

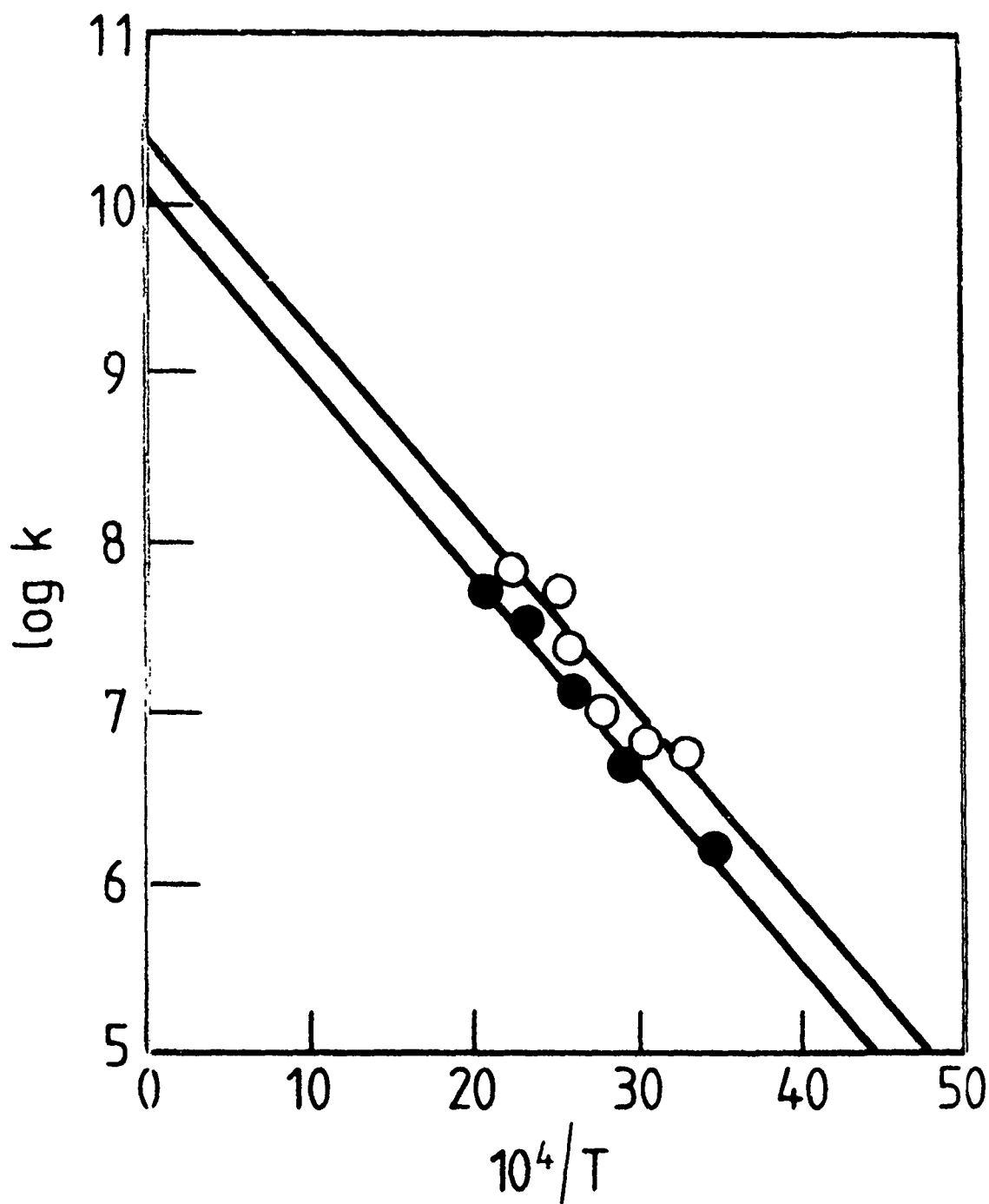


Figure 3. Arrhenius plots for oxygen atom attack.

Full circles: Methyl nitrate

Open circles: Ethyl nitrate

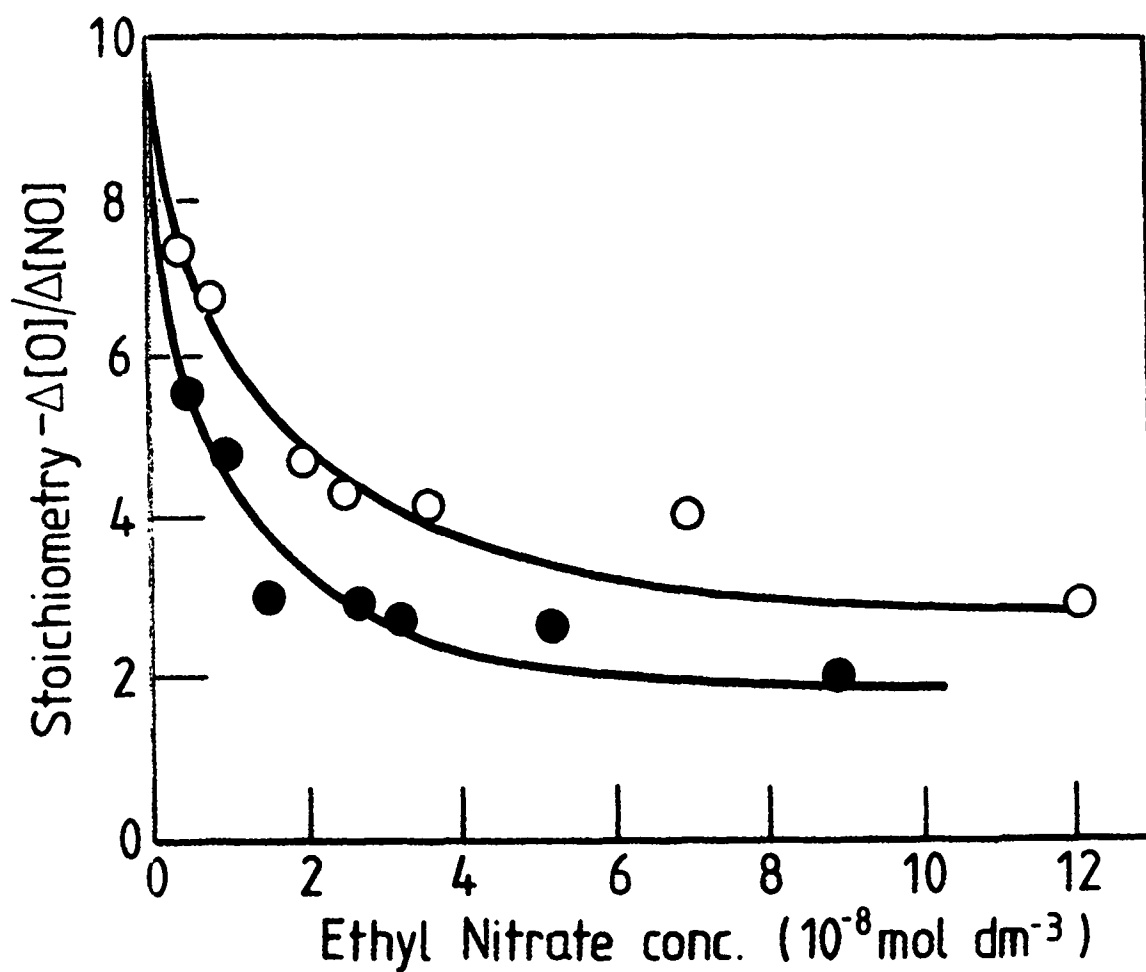


Figure 4. Full circles: 0.30 s reaction time at 300.2K;

$$[O]_0 = 2.7 \times 10^{-7} \text{ mol dm}^{-3}$$

Open circles: 0.25 s reaction time at 333.2K;

$$[O]_0 = 2.5 \times 10^{-7} \text{ mol dm}^{-3}.$$

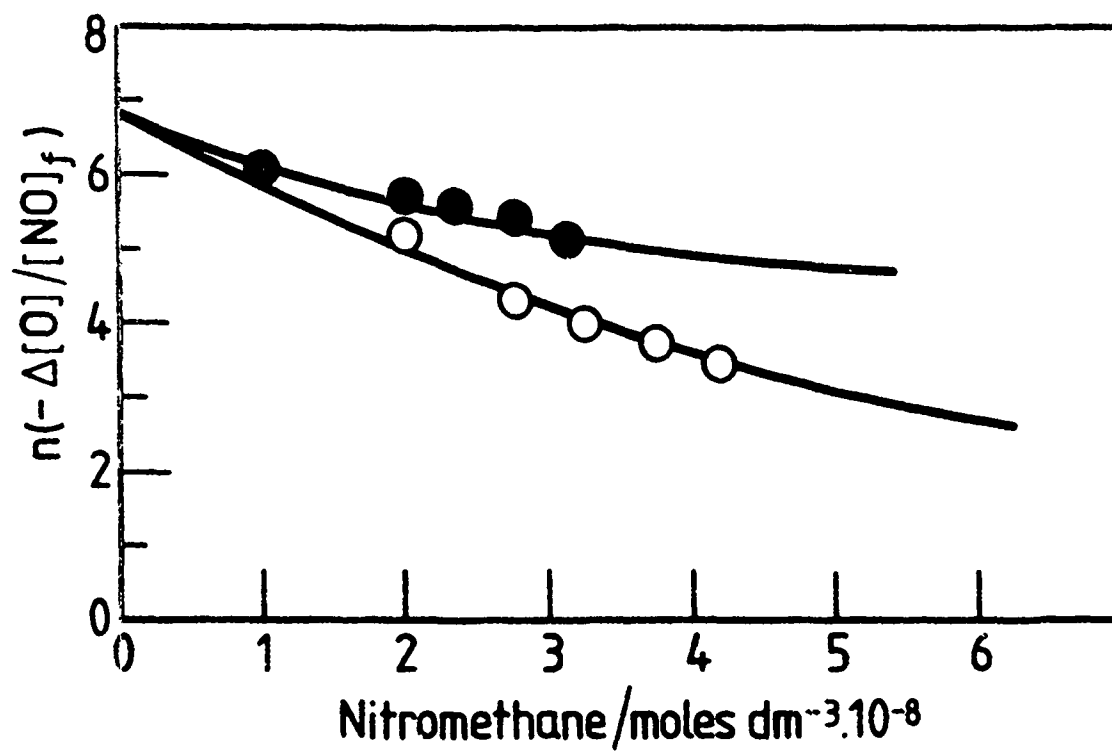


Figure 5. Dependence of reaction stoichiometry on nitromethane concentration.

- 0.1 s reaction time at 294.2K; $[O]_0 = 4.0 \times 10^{-7} \text{ mol dm}^{-3}$.
- 0.23 s reaction time at 423.2K; $[O]_0 = 0.9 \times 10^{-7} \text{ mol dm}^{-3}$.

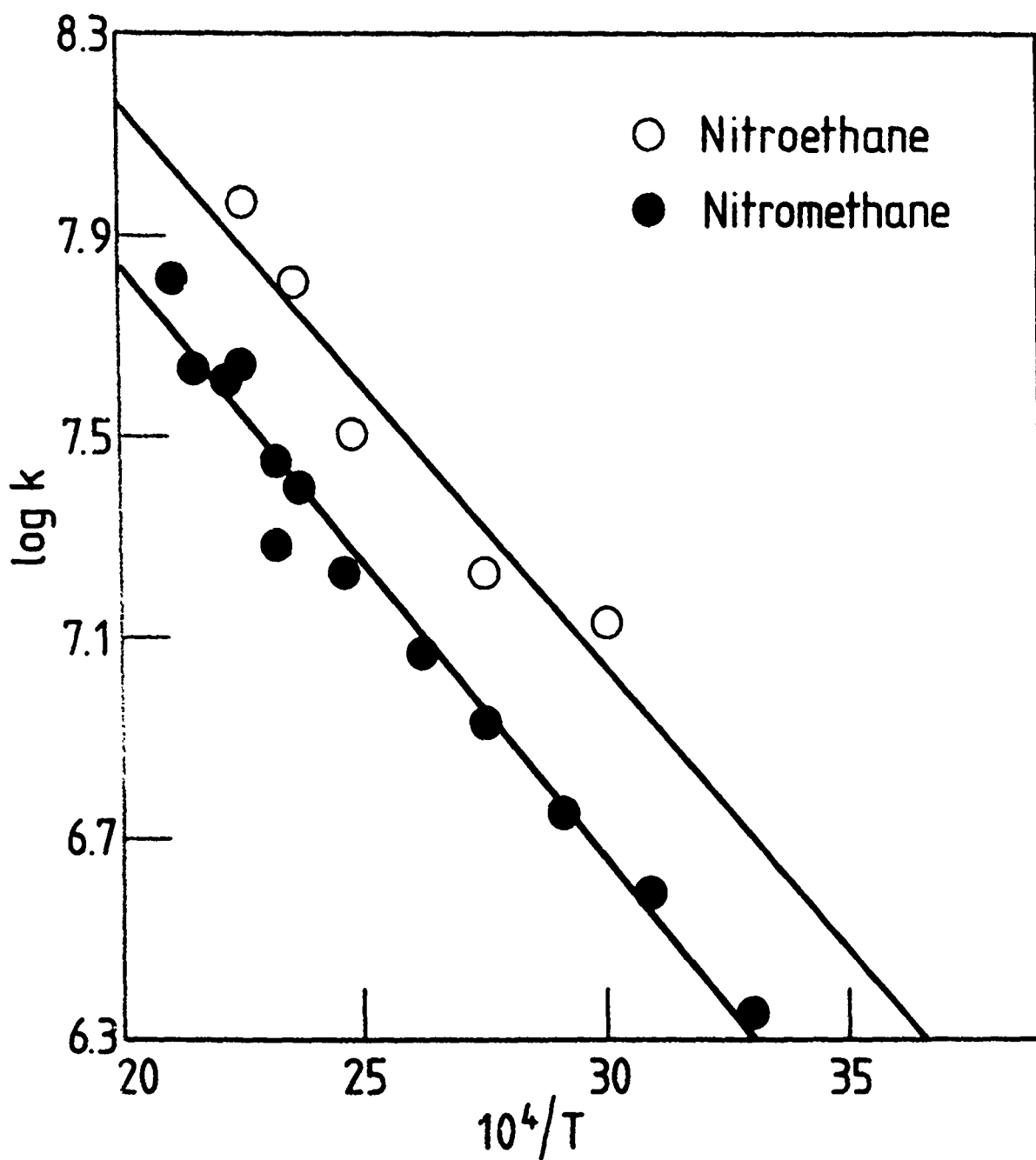


Figure 6. Arrhenius plots for initial attack of oxygen atoms on nitromethane and nitroethane.

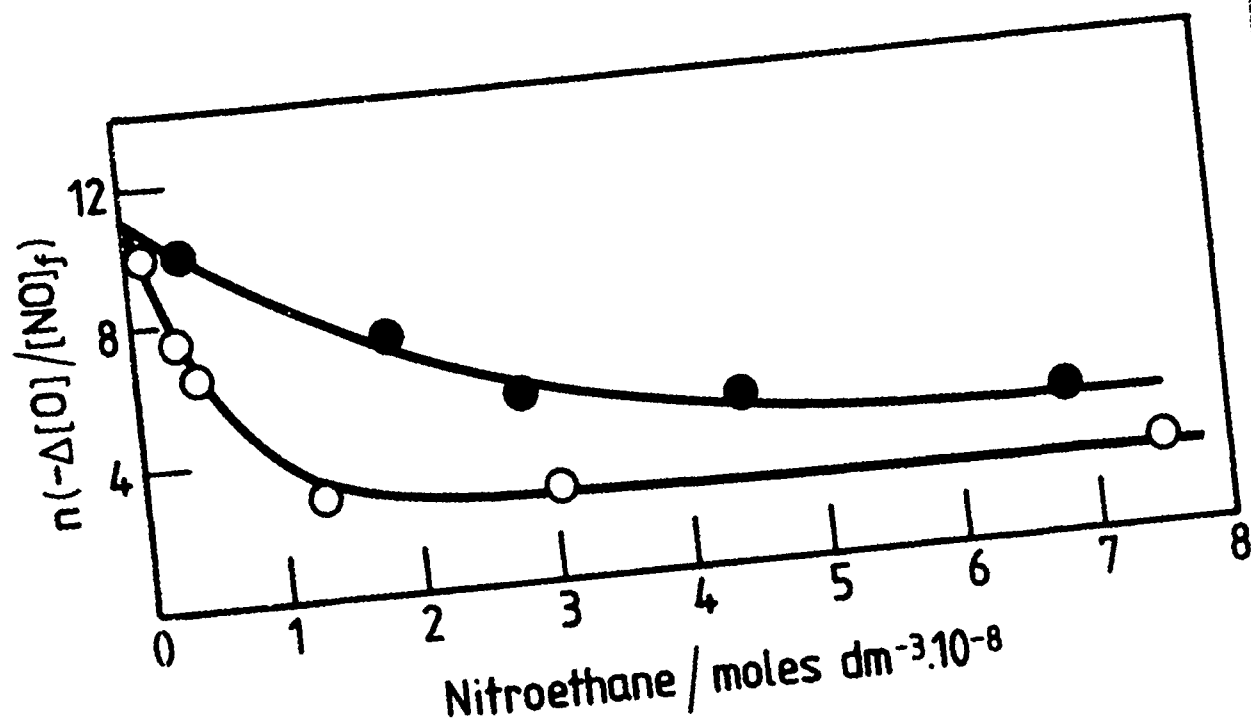


Figure 7. Dependence of reaction stoichiometry on nitroethane concentration

○ 0.2 s reaction time at 473.2K; $[O]_0 = 9.1 \times 10^{-7} \text{ mol dm}^{-3}$.
 ● 0.175s reaction time at 333.2K; $[O]_0 = 5.2 \times 10^{-7} \text{ mol dm}^{-3}$.

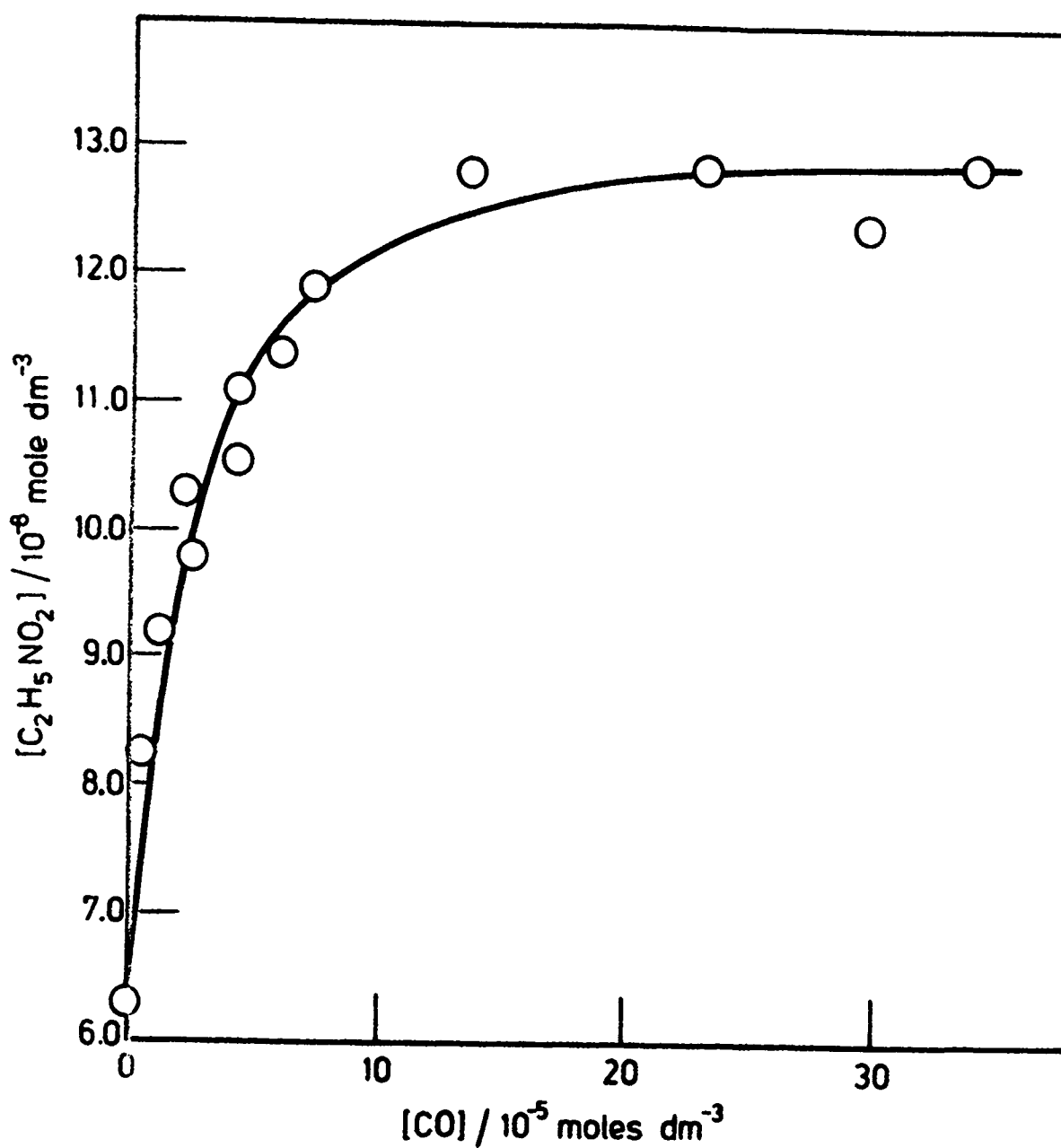


Figure 8. Effect of carbon monoxide on amount of nitroethane required to produce a chain reaction with atomic oxygen at 296K.

$$[O]_0 = 3 \times 10^{-8} \text{ mol dm}^{-3}.$$

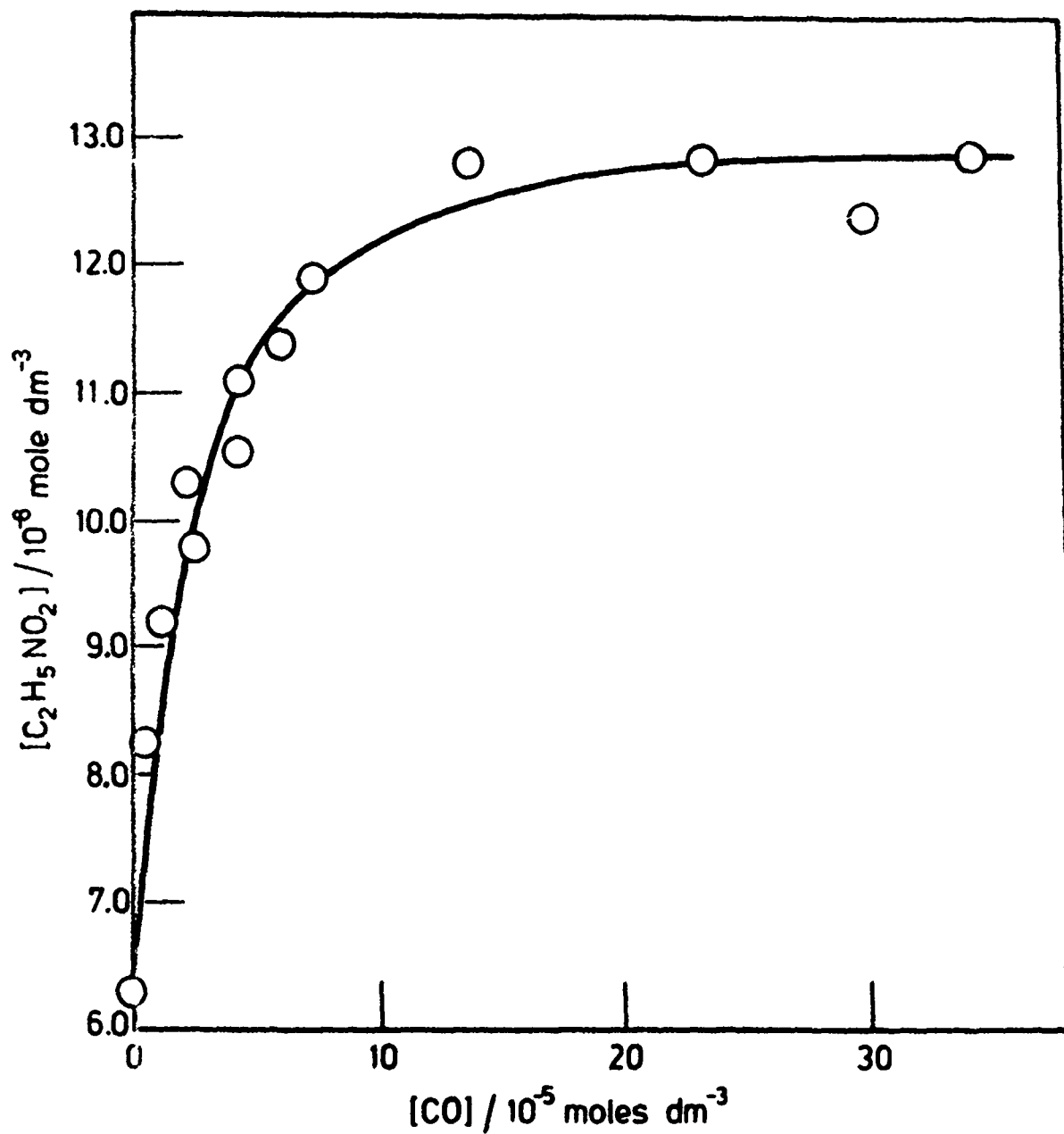


Figure 8. Effect of carbon monoxide on amount of nitroethane required to produce a chain reaction with atomic oxygen at 296K.
 $[O]_0 = 3 \times 10^{-8} \text{ mol dm}^{-3}$.